

Study of Portland cement fracture surfaces by scanning electron microscopy techniques

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An extensive scanning electron microscopy study was carried out with respect to the fracture surfaces of Portland cement hydrated for various times. It is shown that the two major products of hydration are calcium silicate hydrate spherulites, which consist of radiating fibres and calcium hydroxide platelets. These fibres bond with one another to hold the spherulites together. The volume between the spherulites consists of calcium hydroxide platelets. The fracture is frequently found to be across the weakly bonded basal planes of the calcium hydroxide, and is believed to limit the strength of the Portland cement.

1. Introduction

Perhaps the most widely used of all materials is cement, and in particular type I Portland cement. Anhydrous type I Portland cement contains the following components* in the approximate percentages indicated [1]: 45% C_3S (tricalcium silicate, also known as alite), 27% β - C_2S (β -dicalcium silicate), 11% C_3A (tricalcium aluminate), 8% C-A-F, a ferrite phase of variable composition, 3.1% $CaSO_4$ (gypsum), 2.9% MgO and 0.5% free CaO. Assuming, as a first approximation, that the above compounds react with water independently of one another, both C_3S and β - C_2S combine with water to form calcium silicate hydrate [2], also termed C-S-H gel or tobermorite gel along with CH ($Ca[OH]_2$, also termed Portlandite). Whereas C_3S is almost completely hydrated after one month, β - C_2S requires nearly a year for its completion. The reaction of C_3A with water forms a calcium aluminate hydrate or C-A-H and is rapid. The purpose of the gypsum is to slow down the hydration of C_3A .

Since C-S-H gel and CH comprise over 75% of the hydrated Portland cement paste it follows that they must play a major role in determining the strengthening behaviour of cement. In this

respect, it has been postulated [4] that CH represents the weaker of the two phases. In spite of some recent transmission electron microscopy [2, 5] and scanning electron microscopy (SEM) studies [6-10], it has not yet been possible to determine the detailed structure, to say nothing of the strengthening mechanisms of either the tobermorite gel or the calcium hydroxide. For this reason, it was decided to carry out a very high resolution SEM investigation of the fracture surfaces of type I Portland cement paste.

2. Experimental procedure

The type I Portland cement powder used in the present investigation was obtained from the National Sand and Gravel Association and the National Ready Mixed Concrete Association, and consisted of a mixture of three commercially available brands. This cement powder was mixed with distilled water to give a 0.5 water/cement ratio. Because of the difficulty in preparing short hydration time samples for observation within the SEM, owing to crumbling, two methods of preparation were used. For samples to be observed after hydration times of less than three days, a thin layer of cement paste was spread on a SEM specimen stub and covered

* According to standard cement nomenclature [3] C=CaO, S=SiO₂, A=Al₂O₃, F=Fe₂O₃ and H=H₂O.

under pressure with a glass slide. These samples were kept under moist conditions until the time of observation. For samples that were to be hydrated three or more days, the cement was moulded in $1\frac{1}{2}$ in. lengths of $\frac{1}{2}$ in. diameter polyethylene tubing for 24 h under moist conditions, unmoulded, and then kept under water until the time of observation.

After the requisite times, the samples were fractured. In the case of the short time specimens, the fracture was accomplished by simply pulling the glass slide from the specimen stub, and retaining the fracture surface associated with the stub surface. For the longer hydration times, the samples were fractured by bending. In both cases, the samples were dried under vacuum immediately after fracture to ensure that the hydration reactions were terminated almost simultaneously with the fracture, and kept under vacuum until examined in the SEM. The specimens were then coated with an alloy of 60% Au-40% Pd, and their fracture surfaces were subsequently examined within the Cambridge Stereoscan Mark 2A SEM operating at 20 kV. In order to ensure close proximity of the emitted secondary electrons to the detector, the fracture surfaces were usually inclined about 45° to the incident beam.

3. Experimental results and discussion

Fig. 1 shows a scanning electron micrograph of a fracture surface of Portland cement paste which had been hydrated for 1 h. The fracture is seen to be entirely intergranular in nature, consisting essentially of the original unbonded grains which comprised the Portland cement powder. Fig.

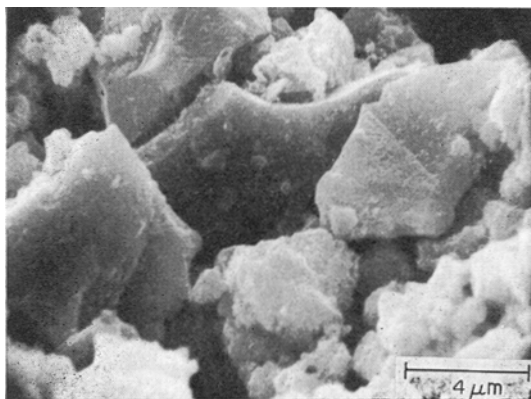


Figure 1 Scanning electron micrograph of the fracture surface of a Portland cement paste after 1 h hydration.

2a, on the other hand, shows that after 24 h, clusters of individual cement grains become covered with a network of intertwining fibres.

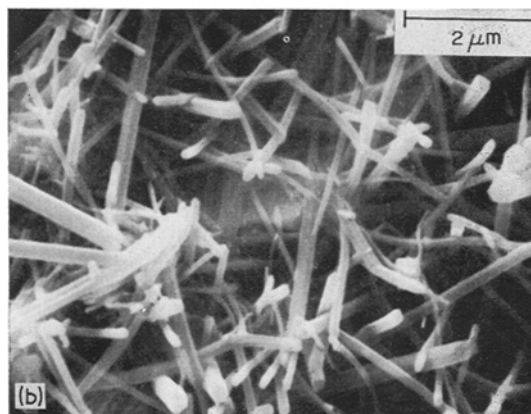
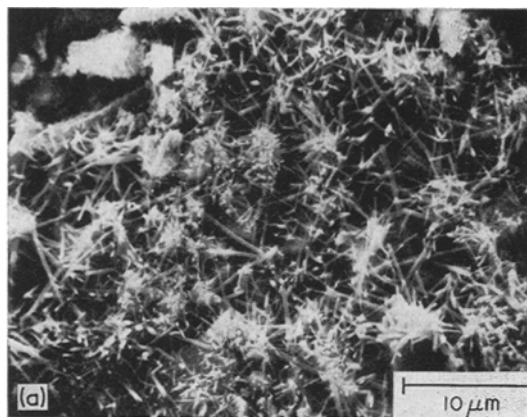


Figure 2 (a) Scanning electron micrograph of the fracture surface of a Portland cement paste after 24 h hydration, showing network of fibres comprising tobermorite gel. (b) Higher magnification micrograph from the centre of the area shown in (a).

The morphology of the fibres is shown in more detail in the higher magnification micrograph of Fig. 2b. They are seen to be on the order of 1000 Å in diameter and quite long as compared to this diameter. Furthermore, the fibres in Fig. 2b are seen to have geometrical cross-sections which can sometimes be identified as square. In many other cases, the fibres are seen to bend and form bonded junctions with one another at their crossing points. All of these features point to the conclusion that the fibre aggregates in Fig. 2 represent the initial formation of the tobermorite

gel product resulting from the hydration of the C_3S particles.

As the hydration time progressed, the density of the fibres comprising the tobermorite gel increased until all areas of the fracture surface were covered with them. In addition, after hydration periods of six days, very well defined flat hexagonal platelets began to form. They increased in number to the extent that, after 21 days, they occupied large areas of the fracture surface. This can be seen by reference to the scanning electron micrograph of Fig. 3a which shows a cluster of hexagonal shaped plates imbedded in a matrix of tobermorite gel. A

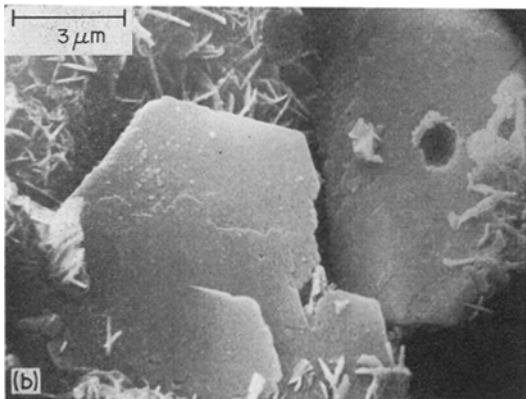
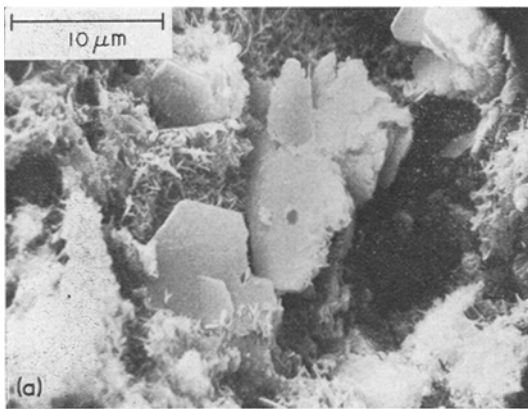


Figure 3 (a) Scanning electron micrograph of the fracture surface of a Portland cement paste after 21 days hydration, showing calcium hydroxide platelets. (b) Higher magnification micrograph from the centre of the area shown in (a).

higher magnification micrograph of the centre of Fig. 3a can be seen in Fig. 3b, where it will be

noted that the flat faces of the platelets consist of terraced layers. An even more striking feature of this layering can be seen in the scanning electron micrograph of Fig. 4 where a number of the layers have been pulled apart, presumably as a result of the fracture process. There seems to be

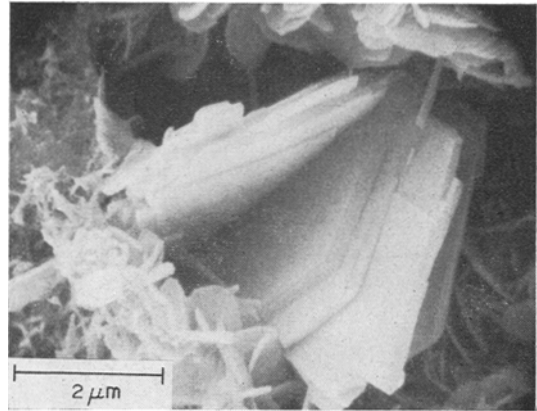


Figure 4 Scanning electron micrograph of the fracture surface of a Portland cement paste after 21 days hydration, showing cleavage through the calcium hydroxide platelets.

little doubt that the hexagonal platelets observed in Fig. 3 and 4 are in fact calcium hydroxide, one of the two major products of the hydration reaction of C_3S and $\beta-C_2S$. The external hexagonal appearance of the plates is also consistent with the hexagonal structure of $Ca(OH)_2$ [11]. This can be more easily seen by reference to Fig. 5 which shows the ion arrangement in the $Ca(OH)_2$ lattice. For simplicity, Ca^{++} and OH^- have been labelled as Ca and OH or OH' , depending upon whether OH lies in the plane immediately above or below the plane of the drawing, respectively. It is seen that the Ca^{++} ions are sandwiched in between two layers of OH^- ions which are presumably held together by strong ionic bonding. On the other hand, each OH^- layer is bounded by a neighbouring layer of OH^- ions. The attraction between these OH^- layers must thus arise from weak secondary Van der Waals type forces, and it is these weak secondary forces which are responsible for the easy cleavage across the basal planes of $Ca(OH)_2$ observed in Fig. 4.

A third distinct morphology resulting from the hydration of Portland cement paste is shown in Fig. 6. This particular micrograph was obtained

Ca - ATOMS IN PLANE OF DRAWING
 OH - ATOMS IN PLANE IMMEDIATELY ABOVE PLANE OF DRAWING
 OH' - ATOMS IN PLANE IMMEDIATELY BELOW PLANE OF DRAWING

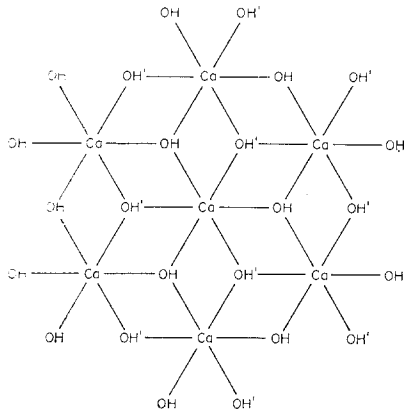


Figure 5 Configuration of Ca^{++} and OH^- ions in the $\text{Ca}(\text{OH})_2$ compound.

after a hydration period of 21 days, although such structures were clearly visible after periods of only three days. This particular morphology will, for convenience, be described as a rosette structure consisting of thin platelets. In addition, unlike the tobermorite gel or the $\text{Ca}(\text{OH})_2$, the rosette structure represents only a small volume fraction of the fracture surfaces observed. It thus seems logical to associate this structure with the product of one of the minor constituents, i.e. calcium aluminate hydrate or the hydrated

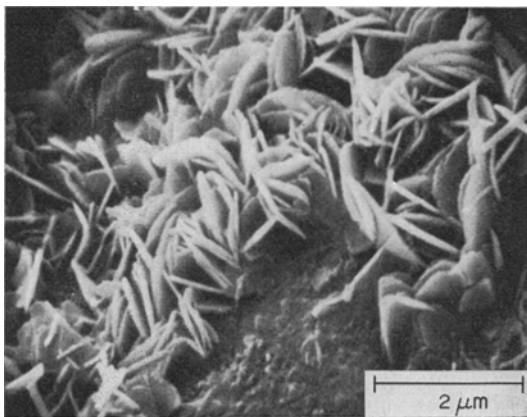


Figure 6 Scanning electron micrograph of the fracture surface of a Portland cement paste after 21 days hydration, showing rosette structure consisting presumably of platelets of calcium aluminate hydrate.

ferrous phase. Since the rosette structure does not seem to play a major role in the strengthening of Portland cement paste, it will not be considered further in the present study. This viewpoint is also supported by the relatively small compressive strength associated with C-A-H and the ferrous phase [2].

It is also interesting to note that the mode of fracture changes as hydration time increases. After short hydration times, the fracture is clearly intergranular, travelling through the water-filled spaces around the grains. By 21 days hydration, transgranular fracture is observed and the amount of transgranular fracture increases thereafter as hydration time lengthens. This could perhaps result from the increased density of the fibres and subsequent increase in bonding between fibres, giving them strength higher than that of the grain. Or, on the other hand, this could result from a change in the nature of the grain itself by hydration, so that it is not as strong as the unhydrated grain.

Having discussed the main morphological features associated with some of the major constituents arising from the hydration of Portland cement, it is next of interest to consider the various aspects of the bonding between these major constituents. In particular, what is the nature of the bonding between the clusters of C-S-H themselves, between the regions of CH themselves and between the regions of C-S-H and CH? It appears logical at this point to anticipate two of the above-mentioned types of bonding to be of the form shown schematically in Fig. 7. In particular, Fig. 7a shows two spherulites of a hydrating C_3S or $\beta\text{-C}_2\text{S}$ particle. The needle-like growth emanating from these particles is the tobermorite gel. The fibres comprising this gel are seen to be interlaced with one another, and the bonding between the two particles arises presumably by the bonding of the individual fibres at their points of intersection, as discussed with respect to Fig. 2. The fibre density decreases radially from the outermost portions of each spherulite to the centre, and the centre may, in fact, consist of unreacted, i.e. unhydrated, C_3S or $\beta\text{-C}_2\text{S}$. The essential correctness of the above model may be verified by reference to the scanning electron micrograph of Fig. 8a which shows a cluster of hydrated calcium silicate spherulites which have intergrown with one another via their fibres in the manner illustrated in Fig. 7a. An even more dramatic scanning electron micrograph showing the

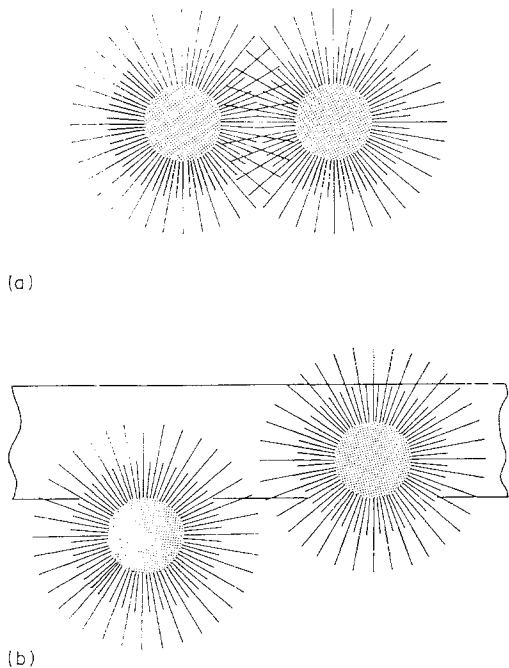


Figure 7 Schematic illustrations showing the bonding between (a) two calcium silicate hydrate particles (b) two calcium silicate hydrate particles with a calcium hydroxide plate.

intergrowth of the outer fibres between adjacent spherulites is shown in Fig. 8b.

The anticipated bonding between the calcium silicate hydrate and the calcium hydroxide is expected to be that illustrated schematically in Fig. 7b. Support for this model has, in fact, been given by the energy dispersion X-ray spectrometry studies of Diamond [7], which has verified the presence of sulphur containing C-S-H fibres within the calcium hydroxide platelets. As in the case of the bonding between individual calcium silicate hydrate fibres, the bonding between these same fibres and calcium hydroxide is unknown, and will have to await a detailed crystallographic analysis of the relationship between the two structures. On the other hand, the scanning electron micrograph of Fig. 9a obtained from the fracture surface of a two-year-old hydrated cement paste shows that fracture and separation has occurred not only through the calcium hydroxide phase, but along the interface between the calcium silicate hydrate and the calcium hydroxide itself. Note that after long hydration times, the fibre density within the tobermorite gel is so great that they cannot be resolved, with the net result that the calcium

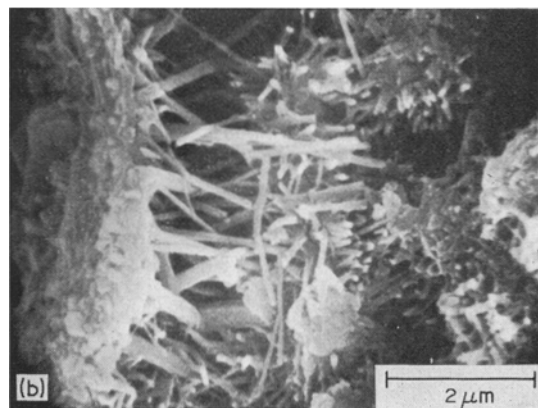
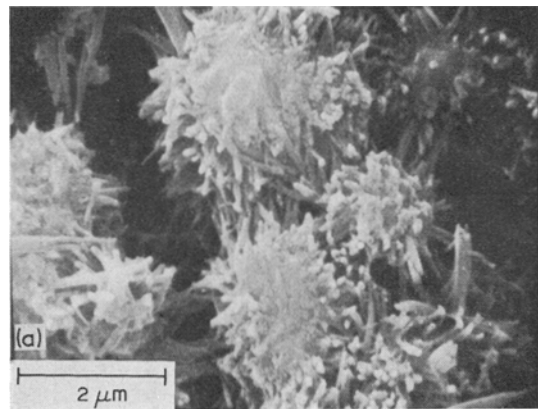


Figure 8 (a) Scanning electron micrograph of the fracture surface of a Portland cement paste after 21 days hydration, showing intergrowth of calcium silicate hydrate fibres from adjacent spherulites. (b) More detailed scanning electron micrograph of the fracture surface from which (a) was obtained, showing intergrowth of calcium silicate hydrate fibres.

silicate hydrate phase appears as a mottled structure. The morphological relationships between the calcium silicate hydrate and the calcium hydroxide is shown in the two-month-old cement paste of Fig. 9b. The right-hand portion of this figure corresponds to the undisturbed region within an interior hole, while the left-hand side of the figure represents the fracture surface. The planar features of the hydroxide and the mottled texture of the C-S-H gel are readily apparent.

No clear-cut observations were obtained to illustrate the nature of the bonding between calcium hydroxide grains. The possible reason

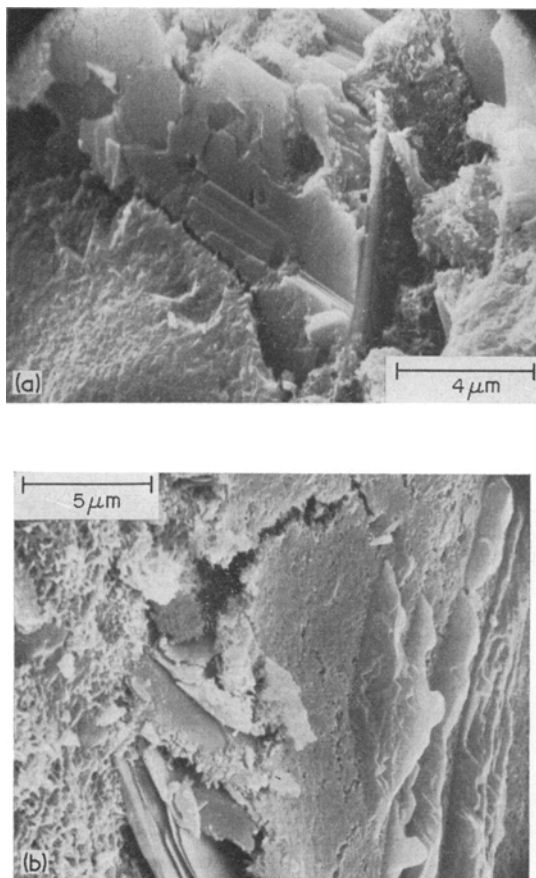


Figure 9 (a) Scanning electron micrograph of the fracture surface of a Portland cement paste after 2 years hydration showing fracture behaviour at the calcium silicate hydrate-calcium hydroxide interface. (b) Scanning electron micrograph of the free surface (right side) and fracture surface (left side) of a Portland cement paste after 2 months hydration, showing the morphological relationships between the calcium silicate hydrate and the calcium hydroxide.

for this is that the hydroxide crystals form as isolated grains in between the interconnected calcium silicate hydrate spherulites, so that the bond between individual calcium hydroxide grains of differing orientation does not play an important role in the fracture behaviour of Portland cement. On the other hand, it is to be emphasized that the weakness of the bonding across the basal planes of the hydroxide plays a major role in limiting the strength of Portland cement. This limitation in strength of calcium hydroxide, however, could be reduced by the strengthening effect resulting from the calcium

silicate fibres imbedded therein as illustrated in Fig. 7b. Also, in the bulk specimen, the calcium hydroxide crystals would be randomly oriented. Therefore, no large uniform cleavage plane would be present which could further reduce the limitation in the strength of calcium hydroxide.

4. Summary and conclusions

A detailed scanning electron microscopy study has been carried out with respect to the hydration behaviour of Portland cement paste as observed on fracture surfaces after various times. In particular, it is shown that after about one day of hydration, the original calcium silicate grains become covered with a dense spherulite network of calcium silicate hydrate fibres, or tobermorite gel, radiating out from the initial unhydrated particles. After 21 days, the fibres from neighbouring spherulites bond with one another. In addition, large plate-like crystals of calcium hydroxide are found in between the spherulites. Both the calcium silicate hydrate, as well as the calcium hydroxide are the products resulting from the hydration reaction of calcium silicate. It is shown that the cleavage through the cement paste occurs mostly across the weakly bonded basal planes of the calcium hydroxide; secondly through the calcium silicate hydrate-calcium hydroxide interface; while the strongest bonding occurs between the calcium silicate hydrate spherulites.

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